## Title

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# Leakage Rates of Refrigerants CFC-12, HCFC-22, and HFC-134a from Operating Mobile Air Conditioning Systems in Guangzhou, China: Tests inside a Busy Urban Tunnel under Hot and Humid Weather Conditions

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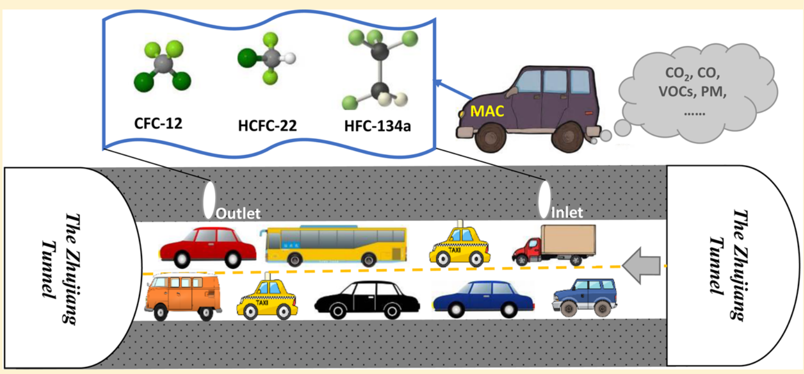
Supporting Information




**ABSTRACT:** Determining the leakage rates of halogenated refrigerants from operating mobile air conditioning systems (MACs) is a challenging task. Here, we take advantage of a heavily trafficked tunnel with a traffic flow of over 40,000 motor vehicles per day in south China. We carried out measurements in 2014 on hot and humid days, and therefore, it is reasonable to assume that essentially all of the MAC units would be turned on to ensure the thermo-comfort of the occupants. Thus, we obtained the leakage rates of the three most important refrigerants from the operating MACs aboard the on-road vehicles. The emission factors (EFs) of HFC-134a, HCFC-22, and CFC-12 from the on-road operating MACs are 1.27 ± 0.11, 0.47 ± 0.04, and 0.17 ± 0.04 mg $km^{-1}$ $veh^{-1}$, respectively. Normalized by the percentages of vehicles using different refrigerants in their MACs, the emission rates of HFC-134a, HCFC-22, and CFC-12 are 52.2, 329, and 59.5 mg $h^{-1}$ $veh^{-1}$, respectively. This emission rate of HFC-134a is approximately 10 times higher than those previously reported in Europe for stationary conditions and a whole-lifetime average of fugitive losses. The unusually high leakage rates suggest that improving the leak tightness of MACs in China would help to greatly lower their emissions. The global warming potentials associated with refrigerant leakage is equal to 1.4% of the $CO_2$ directly emitted due to fuel consumptions.

## INTRODUCTION

CFC-12 ($CCl_2F_2$), HCFC-22 ($CHClF_2$), and HFC-134a ($CH_2FCF_3$) are the most abundant chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) compounds in the Earth's atmosphere, respectively. These compounds have ozone depletion potentials (ODPs) of 1.0, 0.055, and 0 and global warming potentials (GWPs) of 10,900, 1,810 and 1,430, respectively.[1,2] They represent three generations of coolants used in refrigerators, indoor air conditioners, and other refrigeration equipment, such as refrigerated trucks and mobile air conditioning systems (MACs). The emissions and global

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mixing ratios of CFCs have decreased as a result of the phasing out of their production and use under the Montreal Protocol and its Amendments (MPA).[1] HCFCs have been widely used as transitional substitutes for CFCs since the 1990s.[3] They will be phased out by 2030 in developed countries (non-Article 5 countries) and by 2040 in developing countries (Article 5 countries), based on the current Montreal Protocol.[1,4] Hydrofluorocarbons (HFCs), which are the principal replacement compounds for both CFCs and HCFCs, have ODPs of zero but high GWPs. They are instead regulated under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) and the Kigali Agreement (http://www.ccacoalition.org/en/news/historical-agreement-hfcs-reached-kigali, accessed on October 18, 2017), as they contribute to the radiative forcing of the atmosphere.[5] Increases in global HFC-134a emissions and atmospheric mixing ratios have also been observed in response to the success of MPA,[1,6,7] but the contributions of HFCs to global radiative forcing[8,9] and elevated concentrations of persistent trifluoroacetic acid[10,11] are expected to become increasingly significant if HFC emissions continue to rise as projected without any regulation.

However, existing emissions inventories for these important ozone-depleting substances (ODSs) and halogenated greenhouse gases include significant uncertainties, particularly in developing countries. Based on atmospheric models and measurements, Lunt et al.[9] showed that the reported emissions of HFCs from developed countries were consistent with atmospheric measurements; however, almost half of the global emissions originated from nonreporting or non-Annex I countries. This group of countries includes China, which is the largest developing country and produces and consumes the largest amounts of these refrigerants in the world, according to UNEP.[12]

Although emissions of ODSs and halogenated greenhouse gases in China are a source of broad concern, only a few studies that present bottom-up emission inventories are available,[13−16] and top-down estimates are limited to measurements in China's megacities and at numerous background sites.[4,17−21] Some of the emission estimates are far from consistent with each other. For example, Stohl et al.[4,17] estimated that HCFC-22 emissions for China were 71 kt/yr in 2006 and 65.3 kt/yr in 2008. These rates correspond to approximately 16−20% of the global emissions of this compound.[4,22,23] Meanwhile, Vollmer et al.[18] estimated that the HCFC-22 emissions in China in 2007 were 165 kt/yr, which instead corresponds to ~45% of the estimated global emissions of this compound. To reduce the uncertainties in the emission estimates for these coolants, one priority is to accurately characterize their emissions from important sectors, including those from MACs.

As China has become the largest manufacturer of automobiles in the world and the country with the largest market for automobiles, emissions of refrigerants from MACs represent a source of increasing concern. A typical MAC unit may emit refrigerants during its manufacture, operation (including servicing), and end-of-life disposal, with most of this leakage occurring during the operational lifetime of the unit.[15,25] Throughout the in-use phase of MACs, apart from losses that occur during recharging,[26] refrigerants may leak during operation and standstill periods, due to permeation through hoses and diffusion past fittings and seals. These losses are often termed as "regular" leakage, in contrast to "irregular" losses that occur due to accidents, strikes by road debris, or component failures. Refrigerant leakage during on-road operational periods is expected to be much larger than that during the off-road stationary phase, as higher vapor pressures occur during the operation of compressors, and the increased heat stress near the MAC unit likely facilitates losses due to permeation or diffusion.[27] Xiang et al.[6] observed pronounced seasonal variations in global emissions of HCFC-22 and HFC-134a, which are 2−3 times higher in summertime than in wintertime. This result implies a temperature- or use-dependent emission enhancement. While regular annual leakage rates are typically estimated based on the difference in mass between the initial and remaining refrigerants over some time interval, and the refrigerant leakage from stationary vehicles can be measured using a Sealed Housing for Evaporative Determination (SHED) apparatus,[28] it is not easy to obtain measurement-based EFs for refrigerant leakage from MACs under on-road operation conditions.

In this present study, we take advantage of a field campaign that was conducted in June 2014 in the Zhujiang Tunnel (23.11° N, 113.23° E) in urban Guangzhou, south China.[30−32] During this campaign, EFs of CFC-12, HCFC-22, and HFC-134a from the MACs onboard the on-road vehicle fleet were measured. To the best of our knowledge, only one study[29] was carried out in Zürich, Switzerland, to obtain the EFs of refrigerants from road vehicles in tunnel tests. However, as Guangzhou has a subtropical to tropical, hot and humid climate, and our measurements were conducted during hot days at the end of June 2014, MACs inside almost all of the on-road vehicles passing through the tunnel were operating to ensure the thermal comfort of passengers. Therefore, EFs from this study provide a good representation of EFs of refrigerants from MACs under on-road operation modes.

## ■ MATERIALS AND METHODS

**Field Work.** This study was conducted from June 25 to July 1, 2014, in the Zhujiang Tunnel, a busy tunnel that passes under the Pearl River in urban Guangzhou. Trace gases were simultaneously detected with online instruments. 1-h VOC samples were collected in pre-evacuated 2-L electro-polished stainless-steel canisters at a constant flow rate of 66.7 mL $min^{-1}$ using a Model 910 pressurized canister sampler (Xonteck, Inc., CA, USA) on two weekdays and two weekend days. Detailed descriptions of the tunnel, *in situ* field measurements, and sample collection procedures used can be found in our previous studies[31,32] and in Text S1.

Carbon dioxide ($CO_2$) was monitored *in situ* using an eddy covariance system (IRGASON, Campbell Scientific, Inc., UT, USA) with an integrated open-path $CO_2/H_2O$ gas analyzer and a 3-D sonic anemometer.

**Laboratory Analysis.** We analyzed VOCs using a Model 7100 preconcentrator (Entech Instruments Inc., CA, USA) combined with an Agilent 5973N gas chromatography−mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). Briefly, VOCs in air samples were concentrated and injected into the GC-MSD/FID system for quantification after three-stage liquid nitrogen cryogenic trapping. MSD was used in the selected ion monitoring (SIM) mode, and HFC-134a, HCFC-22, and CFC-12 were determined based on MSD signals with target ions of $m/z$ 69, 51, and 85, respectively. Details regarding the instrumentation and parameters, analytical conditions, calibration methods, and quality control and quality assurance procedures can be found elsewhere[34,35] and in Text S1. Carbon monoxide (CO) was measured from canister air samples by gas chromatography.[33]

**EF Calculations for Individual Refrigerants.** The average EF of individual refrigerants from vehicles passing through the


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**Table 1. Mixing Ratios and EFs (mg $km^{-1}$ $veh^{-1}$) of Refrigerants from On-Road Vehicles**

| | Mixing ratios (ppt) | | | | | |
|---|---|---|---|---|---|---|
| Compounds | Entrance | Exit | Total average EFs | Global Background (pptv)[a] | ODP-eq $km^{-1}$ $veh^{-1}$[b] | $CO_2$-eq $km^{-1}$ $veh^{-1}$[c] |
| HFC-134a | 116 ± 20[d] | 677 ± 54 | 1.27 ± 0.11 | 77 ± 6 | 0 | 1727 |
| HCFC-22 | 416 ± 32 | 645 ± 33 | 0.47 ± 0.04 | 229 ± 6 | 0.026 | 837 |
| CFC-12 | 554 ± 12 | 593 ± 34 | 0.17 ± 0.04 | 523 ± 1 | 0.17 | 1751 |

[a]Global background data from Advanced Global Atmospheric Gases Experiment (AGAGE) in June 2014 were used, http://agage.mit.edu/data/agage-data. [b]ODP: values from ozone-depleting substances (ODSs) and other gases of interest to the Montreal Protocol.[1] [c]100-yr $CO_2$ equivalent global warming potential (GWP) values from IPCC Fourth Assessment Report.[2] [d]Uncertainties here refer to 95% confidence interval.

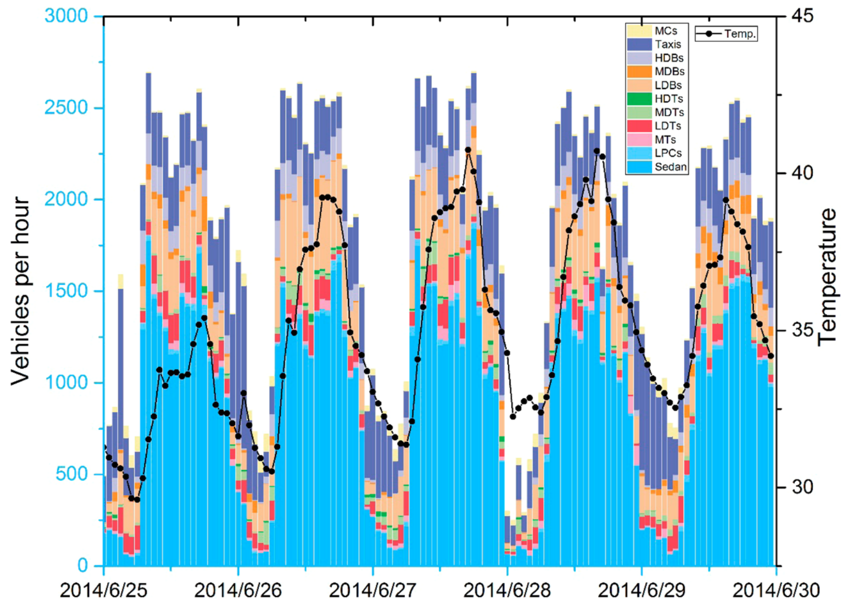


**Figure 1.** Composition of 11 categories vehicle fleet and temperature (°C) variations during campaign.

tunnel during a time interval $T$ is calculated as follows:[31,32]

$$EF_i = \frac{(C_{outlet,i} - C_{inlet,i}) \times V_{air} \times T \times A}{N \times L} \quad (1)$$

where $EF_i$ (mg $km^{-1}$ $veh^{-1}$) is the mean EF of refrigerant $i$ during time interval $T$ (s; 1 h in this study); $C_{outlet,i}$ and $C_{inlet,i}$ (mg $m^{-3}$) are the paired average concentrations of refrigerant $i$ measured at the outlet station and inlet station during the same time interval, respectively; $V_{air}$ (m $s^{-1}$) is the air velocity parallel to the tunnel measured by the 3-D sonic anemometer; $A$ ($m^2$) is the tunnel cross-section area; $N$ is the total number of vehicles passing through the tunnel during the specified time interval, and $L$ (km) is the length of the tunnel between the outlet and inlet stations.

## RESULTS AND DISCUSSION

**Emission Fctors.** The average mixing ratios of HFC-134a, HCFC-22, and CFC-12 at the exit were significantly higher than those at the entrance (Table 1), which means that these refrigerants were emitted from sources in the tunnel. The average mixing ratios of HFC-134a and HCFC-22 at the entrance were 116 ± 20 and 416 ± 32 ppt, respectively. These values are higher than the corresponding values of 84 and 209 ppt measured at the entrance to the Gubrist tunnel in Switzerland in 2002.[29] Similar levels of CFC-12 were measured in this study (554 ± 12 ppt) as were observed in the Gubrist tunnel (559 ppt), even though global levels of CFC-12 have declined by approximately 20 ppt since 2002.[1] These results indicate a relatively large enhancement over background levels for the Zhujiang tunnel. The mean daily number of motor vehicles passing through the tunnel is 42,932 ± 2,235 (mean ±95% C.I.). The average EFs of HFC-134a, HCFC-22, and CFC-12 measured for the road vehicle fleet were 1.27 ± 0.11, 0.47 ± 0.04, and 0.17 ± 0.04 mg $km^{-1}$ $veh^{-1}$ (Table 1), and these values are 18, 78, and 15 times of those measured in the Gubrist tunnel in Switzerland in 2002 (Figure S1),[29] respectively. CFC-12 and HFC-134a are mainly used in passenger cars and buses, whereas HCFC-22 is mainly used in transport/refrigerator trucks. Although CFC-12 has been banned as a refrigerant in newly produced MACs since January first, 2002, CFC-12 is still consumed and used in the servicing of cars produced before 2002.[14,24] Therefore, we still observe emission of CFC-12 in our campaign in 2014 due to the use of MACs in older cars. HFC-134a showed diurnal variations that are similar to those of the number of passenger cars in the Zhujiang tunnel, indicating that HFC-134a was the primary refrigerant used in MACs onboard most of the passenger cars (Figure S2). No significant diurnal variations in the emission factors of CFC-12 or HCFC-22 were observed.

Time series of the vehicle fleet composition in the tunnel during our campaign are shown in Figure 1. Because the Zhujiang tunnel is very busy (over 40,000 motor vehicles pass through it per day), the results of our four-day (two working days and two weekend days) monitoring campaign should be statistically representative. Moreover, as our field campaign was conducted on hot (27−41 °C) (Figure 1) and humid (RH > 82%) days in a densely populated urban area, all of the motor vehicles traveling through the tunnel had their MACs turned on to ensure thermal comfort of the passengers. Our measured EFs thus represent the


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leakage rates when MACs are operated under on-road conditions. Compared to motor vehicles that are parked under standstill conditions, vehicles that are being driven should display substantially higher losses of refrigerant from their MACs, even when the MACs are turned off, as all of the components and connecting lines are exposed to engine vibrations and heat. In addition, when MACs are turned on, additional loss are expected to occur due to the higher pressures generated by the compressors within MACs. This may partly explain why EFs obtained in our study are much higher than those measured in the Gubrist tunnel in Switzerland in September–October 2002.[29] During that campaign, the weather was much more thermally comfortable, and it is likely that not all of the motor vehicles had their MACs turned on.

Given the relative GWPs of HFC-134a, HCFC-22, and CFC-12, the calculated $CO_2$-eq emissions that resulted from the emissions of these refrigerants reach 1816, 851, and 1853 mg $CO_2$-eq km$^{-1}$ veh$^{-1}$, respectively. Moreover, considering the average EFs of $3.22 \times 10^5$ mg km$^{-1}$ veh$^{-1}$ for $CO_2$ measured during the corresponding time intervals in this same campaign, the $CO_2$-eq emissions due to the losses of refrigerant from the road vehicles corresponds to 1.4% of the $CO_2$ directly emitted by the vehicles due to their fuel consumption. The time during which vehicles are driven is much less than the time they spend parked, and MACs operate during only a fraction of the driving time, depending on climatic conditions. A previous study[28] showed that the $CO_2$-eq emissions that result from the leakage of HFC-134a from stationary vehicles with their engines and air conditioning (A/C) systems turned off may correspond to approximately 4–5% of the $CO_2$ emitted directly from vehicles. This percentage is much higher than the value for on-road vehicles with their engines and A/C systems turned on presented in our results (1.4%). Therefore, if other regular and irregular emissions and the additional fuel consumption due to MAC operation are taken into account, the $CO_2$-eq emissions from the transportation sector due to MAC operation are considerable and non-negligible.

**Implications.** To the best of our knowledge, no published data describes the leakage rates from MACs during their operation. As mentioned above, we measured average road vehicle fleet EFs of $1.27 \pm 0.11$, $0.47 \pm 0.04$, and $0.17 \pm 0.04$ mg km$^{-1}$ veh$^{-1}$ for HFC-134a, HCFC-22, and CFC-12, respectively, and these values represent times when MACs were operating. Given the average driving speed of 35.0 km h$^{-1}$ during the sampled time intervals, we can convert the total fleet EFs to 44.5, 16.5, and 6.0 mg h$^{-1}$ veh$^{-1}$ for HFC-134a, HCFC-22, and CFC-12, respectively. According to the official statistics data for registered motor vehicles in Guangzhou in 2014, we can roughly assume that 85%, 5%, and 10% of the vehicles in the road vehicle fleet used HFC-134a, HCFC-22, and CFC-12 as refrigerants in their MACs, respectively (Text S2). Thus, we obtain percentage-adjusted EFs of 52.2, 329, and 59.5 mg h$^{-1}$ veh$^{-1}$ per MACs for HFC-134a, HCFC-22, and CFC-12, respectively.

Although the accurate measurement of HCFC-22 emissions in the tunnel might be made more complicated by additional emissions from cold-chain logistics refrigerator trucks, HFC-134a and CFC-12 were largely related to emissions from MACs. Compared to the leakage rate of HFC-134a of $3 \pm 3$ mg h$^{-1}$ veh$^{-1}$ from 28 A/C-equipped cars in a stationary condition[28] or the average fugitive losses of $6.05 \pm 0.5$ mg h$^{-1}$ veh$^{-1}$ from the A/C units of 300 passenger cars in Europe over their entire lifetime under both stationary and on-road conditions,[27] the HFCs-134a emission rates of ~50 mg h$^{-1}$ veh$^{-1}$ measured in our study are unusually high. These elevated EFs, which are about 1 order of magnitude higher, cannot be fully explained by the pressure increases that occur when MACs are turned on.[28] According to a study by Siegl et al.,[28] the pressure usually increases from 50 to 100 psi when the A/C is turned off to a typical value of 200–400 psi when the A/C is turned on, and the EFs of HFC-134a increase from $0.07 \pm 0.07$ g/day when the A/C is turned off to $0.08 \pm 0.07$ g/day when the A/C is turned on. Thus, an approximately 14.3% increase occurs due to pressure rise. Therefore, further efforts are needed to improve the leak tightness of MACs in China through improving maintenance practice. It is also worth noting that although Wan et al.[13] projected that the number of vehicles with CFC-12 air conditioners would become negligible in China in 2014 our study reveals that the replacement of CFC-12 in MACs has not been complete, even in China's most developed megacities.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00445.

Description of the experimental method (Text S1); estimating percentages of vehicles using HFC-134a, HCHC-22, and CFC-12 in their MACs (Text S2); comparison emission factors of refrigerants from MACs in the Zhujiang Tunnel in 2014 with those in the Gubrist Tunnel, Switzerland, in 2002 (ref 29) (Figure S1); and diurnal variations of MAC EFs and vehicle numbers in the Zhujiang Tunnel (Figure S2). (PDF)

Original concentrations in entrance and exit stations (XLSX)

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### Notes

The authors declare no competing financial interest.

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